**CVD in a trench - step coverage - to estimate sticking coefficients**

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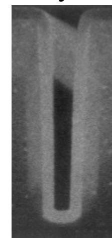
Komiyama et al. [*Chem. Eng. Sci.* **54**, p. 1941 (1999)] consider film deposition in a trench or cavity in a patterned surface. This relates to the term "step coverage" in patterning wafers.



Synonyms for current purpose: step, trench, cavity, hole.

Steps and trenches are made by masking, patterning and etching wafers. By measuring the thickness of films deposited vs. depth in a trench during CVD, one can estimate the values of reaction rate coefficients. Those rate coefficients can be then used in mathematical models of CVD processes.

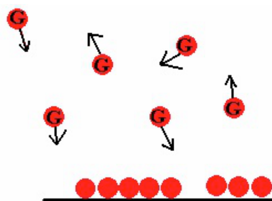
In section 2.2.1, they write equations for film deposition on the walls of a cylindrical hole in a wafer surface as a model system. This is interesting because of the similarity of the equations to diffusion and reaction in a porous solid catalyst. The model is going to need a reaction rate coefficient and diffusion coefficient.

They consider a 1st-order rate equation for film deposition. In order to keep track of terms in equations so that we don't leave something out, write units for the terms, at least at the start and end of equation development.

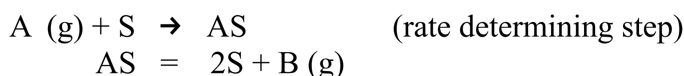
$$r(\mathrm{mol/m^2/s}) = k_s(\mathrm{m/s})\, C_A(\mathrm{mol/m^3})$$

where $C_A$ is the concentration of the gas-phase component, let's call it A, that is reacting over the surface to produce the solid film.

They use a "sticking coefficient" of gas molecules striking a surface. They relate the sticking coefficient to the surface rate coefficient.



In order to see how a sticking coefficient is involved, consider the following kinetic model for the reaction.



A (g) + S → AS (rate determining step)

AS = 2S + B (g)

A (g) → S (s) + B (g) (overall stoichiometric equation)

For this kinetic model, the rate of reaction is equal to the rate of adsorption of gas-phase component A. The rate of adsorption can be described in terms of the rate at which gas molecules collide with the surface and the fraction of those that collide that adsorb.

$$-r_A(\text{mol/m}^2/\text{s}) = r_S = r_{ads} = \left(\frac{Z(\#/\text{m}^2/\text{s})}{N_{AV}(\#/\text{mole})}\right)\eta = \left(\frac{Z(1/\text{m}^2/\text{s})}{N_{AV}(1/\text{mole})}\right)\eta$$

where $Z$ is the "collision frequency" per unit area and $\eta$ is the sticking coefficient, which is equal to the fraction of the molecules hitting the surface that adsorb or "stick." The # symbol above is number of molecules and usually is left out of when units are written, as shown in the last term.

The sticking coefficient will be a function of the extent of coverage of the surface by adsorbed species. For example, in Langmuir-Hinshelwood models of surface reaction kinetics we often assume a linear dependence of the sticking coefficient on surface coverage:

$$r_{ads} = k_{ads} C_A \theta_S = k_{ads} C_A (1 - \theta_{AS})$$

$$r_{ads} = \left(\frac{Z}{N_{AV}}\right)\eta = \left(\frac{Z}{N_{AV}}\right)\eta_0 (1 - \theta_{AS})$$

$$k_{ads} C_A = \left(\frac{Z}{N_{AV}}\right)\eta_0$$ where $\eta_0$ is the "initial sticking coefficient"

This linear dependence of the sticking coefficient on coverage is often used as a model although the real behavior is more complex (see Kisliuk model of adsorption for a more realistic model).

The "kinetic theory of gases" can be used to get expressions for the collision frequency.

$$Z = \frac{P}{\sqrt{2\pi m k_B T}}$$ "Hertz-Knudsen equation"

$$= \frac{1}{4}\left(\frac{n N_{AV}}{V}\right)\sqrt{\frac{8 R_g T}{\pi M}}$$

$$= \frac{1}{4}\left(\frac{n N_{AV}}{V}\right)\bar{v}$$

where $m$ = mass of molecule (kg), $k_B$ = Boltzmann constant, $T$ = temperature (K), $n$ = number of moles, $N_{AV}$ = Avagadro's number (#/mol), $V$ = volume of gas (m$^3$), $R_g$ = ideal gas constant, $M$ = molecular weight of gas component (kg/mol), $\bar{v}$ = mean velocity of gas molecules (m/s). $R_g = k_B N_{AV}$, and $M = m N_{AV}$. This equation is consistent with the ideal gas equation of state (ideal gas law).

For $N_2$ at 1 mbar and 20°C, $Z = 2.9 \times 10^{24}$ (#/m$^2$/s). There are about $1.2 \times 10^{19}$ surface atoms per m$^2$ for a typical material, so this is a collision rate of $2.6 \times 10^5$ collisions per surface atom per second at 1 mbar. At $10^{-9}$ bar = $10^{-4}$ Pa, the collision rate is 0.26 collisions per surface atom per second. This is a typical pressure in an ultra-high vacuum system used to study surface chemistry over clean surfaces.

The "Hertz-Knudsen" equation was written as "Hearts-Knudsen" by Komiyama et al. The word "Herz" in German translates to "heart" in English, so this is an inadvertent and mistaken play on words.

$$C_A = \frac{n_A}{V}$$

$$k_{ads} C_A = k_{ads} \frac{n_A}{V} = \left( \frac{Z}{N_{AV}} \right) \eta_0 = \frac{1}{4} \left( \frac{n_A}{V} \right) \bar{v} \eta_0 = \frac{1}{4} \bar{v} \eta_0 C_A$$

$$k_{ads} = \frac{1}{4} \bar{v} \eta_0$$

$$r_S = k_{ads} C_A (1 - \theta_{AS}) = \frac{1}{4} \bar{v} \eta_0 C_A (1 - \theta_{AS})$$

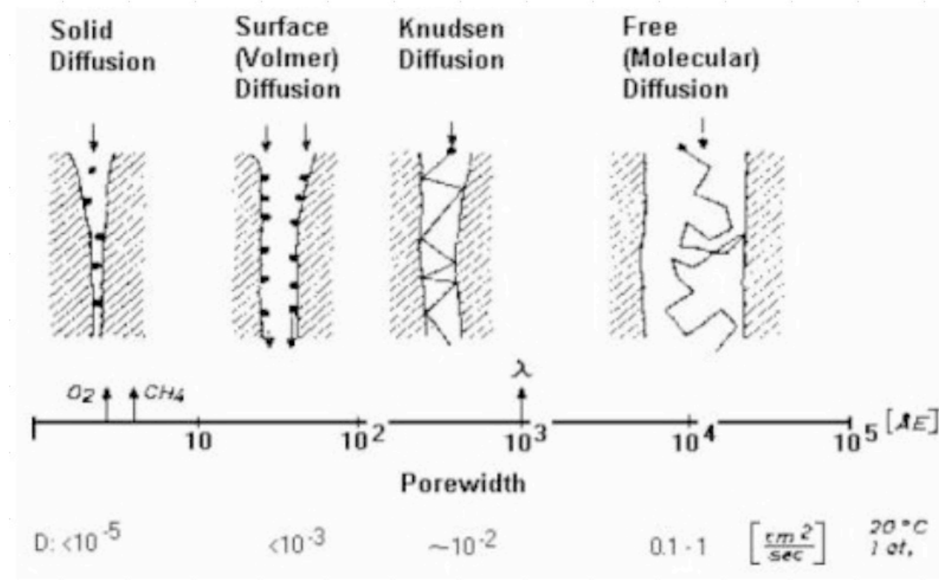
At low coverages of the adsorbed reactant, the reaction will be 1st-order in A,

$$r_S = k_{ads} C_A = k_S C_A = \frac{1}{4} \bar{v} \eta_0 C_A \quad \text{for} \quad \theta_{AS} \ll 1, \text{ and}$$

$$k_S = \frac{1}{4} \bar{v} \eta_0$$

which is Komiyama et al. Equation (6d). So we have the reaction rate coefficient in terms of the mean velocity of gas molecules and the sticking coefficient.

Now we need an expression for the diffusion coefficient. Komiyama et al. considered cases where the distance that gas molecules travel between collisions with other molecules is larger than the width of the trenches in the wafers. When this happens, the gas molecules diffuse by colliding only with the walls of the trench and not with other gas molecules. This mode of diffusion is called "Knudsen diffusion."

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Knudsen diffusion happens in gas at relatively low pressure that is contained within relatively small pores, channels or trenches in this case. The kinetic theory of gases gives the "mean free path" of gas molecules.

$$\bar{l}\,(\mathrm{m}) = \frac{k_B T}{P d^2 \pi \sqrt{2}}$$

where $d$ is the diameter of the gas molecules. The mean free path increases as pressure decreases. For $N_2$ at 20°C and 1 bar, the mean free path is 60 nm. At 1 mbar, the mean free path is 60 µm. Fig. 16 in Komiyama et al. shows that the trench widths they used was 0.5-3.0 µm. So reactant gas at 20-120 mbar would undergo Knudsen diffusion in the trenches because the deposition temperature would be higher than 20°C.

When Knudsen diffusion applies, the Knudsen diffusion coefficient is given by the kinetic theory of gases,

$$D_K = \frac{1}{3} W \bar{v} \quad \text{which is Komiyama Equation (6c)}$$

$$= \frac{W}{3} \sqrt{\frac{8 R_g T}{\pi M}}$$

where $W$ is the diameter of a cylindrical pore, using the notation of Komiyama et al. $D_K$ is independent of pressure and proportional to the square root of temperature.

Now we have expressions for the 1st-order surface reaction rate constant and the diffusion coefficient in a trench for low pressure CVD.

For a small diameter hole in the wafer, we can safely assume that the gas concentration doesn't vary across the diameter so that we can just write a balance for the variation of gas concentration with distance down into the hole. Middleman and Hochberg used this assumption for negligible variation of gas concentration between wafers in the wafer stack LPCVD reactor. In fact, because the mean free path of the gas is larger than the diameter $W$, there can be no variation in concentration across the diameter!

$$D\,(\mathrm{m^2/s}) \frac{d^2 C\,(\mathrm{mol/m^3})}{dz^2\,(\mathrm{m^2})} - \frac{S\,(\mathrm{m^2})}{V\,(\mathrm{m^3})} k_S\,(\mathrm{m/s})\, C\,(\mathrm{mol/m^3}) = 0 \quad \left[\frac{\mathrm{mol}}{\mathrm{m^3\,s}}\right]$$

$$D \frac{d^2 C}{dz^2} - \frac{S}{V} k_S C = 0 \quad \text{which is Komiyama Equation (5a)}$$

The depth of the trench or hole is $H$. The surface to volume ratio, $S/V$, for a cylindrical hole is $4/W$. For a trench $S/V = (2H + W)/HW$. For a high aspect ratio ($H/W$) trench, $S/V = 2/W$.

Making the equation dimensionless,

$$\frac{d^2\psi}{d\lambda^2} - \phi^2\psi = 0 \quad \text{where} \quad \psi = \frac{C(z)}{C(z=0)} \quad \text{and} \quad \lambda = z/H$$

This is the same dimensionless equation that we wrote for a 1st-order reaction in a 1D, "slab geometry" porous solid catalyst layer.

The Thiele modulus for this CVD trench problem is

$$\phi = H\sqrt{\frac{S}{V}\frac{k_S}{D}}$$

using the expressions above for $k_S$ and $D = D_K$ ,

$$\phi = H\sqrt{\frac{S}{V}\frac{1}{4}\bar{v}\eta_0\frac{3}{W\bar{v}}} = H\sqrt{\frac{S}{V}\frac{3}{4}\frac{\eta_0}{W}}$$

using $S/V = 2/W$ for a trench

$$\phi = \frac{H}{W}\sqrt{\frac{3\eta_0}{2}} \quad \text{which is Equation (6b)}$$

The boundary condition at the wafer surface is,

$\psi = 1$ at $\lambda = 1$ which is Equation (5c) in dimensionless form

The boundary condition at the bottom of the trench is that the diffusion rate is equal to the reaction rate at the bottom of the trench, Equation (5b) in dimensionless form,

$$\left[\frac{d\psi}{d\lambda}\right]_{\lambda=0} = Da_S\psi \quad \text{where} \quad Da_S = \frac{k_S}{(D_K/H)}$$

$Da_S$ is a Damkoehler number, which is a dimensionless reaction rate constant. Somewhat like, and related to, the Thiele modulus squared, it is a ratio of a reaction rate constant to a diffusion coefficient.

This is a different boundary condition than the zero-flux BC we used for diffusion and reaction in a porous catalyst:

$$\left[\frac{d\psi}{d\lambda}\right]_{\lambda=0} = 0$$

where we got the solution for $\psi$ as a function of $\lambda$

$$\psi(\lambda) = \frac{\cosh(\lambda\phi)}{\cosh(\phi)}$$

With the reaction-rate BC at the trench bottom, Komiyama et al. get a more complex solution, given in their Equation (6a).

Now what? We want to use results from experiments to estimate the value of the sticking coefficient $\eta_0$ .

The reaction rate is a function of depth $\lambda$ into the trench.

$$r(\lambda) = k_s C_0 \psi(\lambda) \quad [\text{mol/m}^2\text{/s}]$$

and we know $\psi(\lambda)$

So we can run the reaction for a while, then section the wafer and measure the film thickness as a function of depth in the trench. The film thickness is the integrated rate of reaction over the time of the experiment. This is straight forward as long as $W$ doesn't decrease significantly over the time of the experiment as the film grows, thus, changing $\phi$ and our solution. If *W* does change significantly, then we just have to solve for that case, or start with a wider trench.

In order to get an experimental result that is sensitive to the value of the sticking coefficient, we need to have conditions (*T, P, W, H*) such that the film thickness varies down into the trench. We might want to make a test wafer with trenches of different *W* and *H*, and/or do experiments at different *T* and *P*. Note that T and P do not appear explicitly in the equations. However, sticking coefficients can vary with *T* and we should do experiments at different *P*: if there is no variation with *P*, then the assumptions in our derivation are valid.

Figure 13 in Komiyama et al. is a plot of "step coverage" as a function of sticking probability for different aspect ratio = *H/W*. The value of "step coverage" is the ratio of the film thickness at the bottom of the trench to the film thickness at the wafer surface.

The desired value for circuit production purposes is one - we want uniform film coverage of the circuit features - but for our experimental purposes, we want a value less than one such that we can extract the value of the sticking coefficient. For the case with the reaction rate BC at the trench bottom,

$$\text{step coverage} = \psi(\lambda = 0) = \frac{1}{\cosh\phi + \left(\frac{2\text{W}}{H\phi}\right)\sinh\phi}$$

For Aspect Ratio = *H/W* = 5.0 and for sticking probability = $\eta_0$ = 0.1, $\phi$ = 1.94, and the step coverage = 0.24, which is the value we can read off of Figure 13.

So, finally, if we did an experiment with this aspect ratio and measured a step coverage of 0.24, then we would get the value of 0.1 for the initial sticking coefficient. At 1 mbar and 250°C, the collision frequency is $3.5 \times 10^5\ s^{-1}$ per surface atom. Every 10 collisions would deposit a new surface atom. A Si atom has a diameter of $1 \times 10^{-10}$ m. So the film growth rate would be 3.5 μm/s. That is a very fast growth rate. We could lower this rate by working at a lower pressure. Lowering the pressure would lower the rate but would not affect the Thiele modulus value or the step coverage, if the assumptions

used in the derivation apply. I suspect most sticking coefficients are smaller than 0.1.

Section 2.3.1 considers a related system. See the figures below from Komiyama et al.

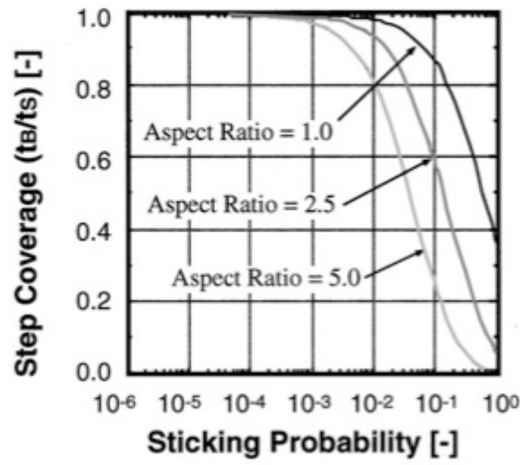


Fig. 13. Relation between step coverage and surface sticking probability.

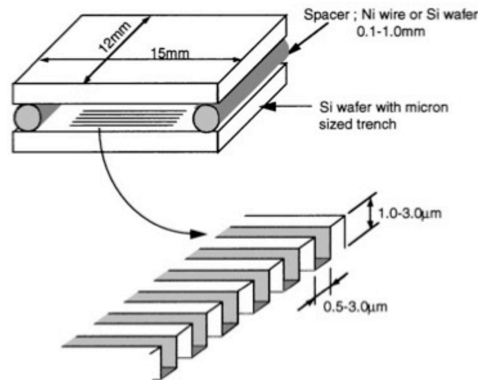


Fig. 16. Structure of a micro/macrocavity.

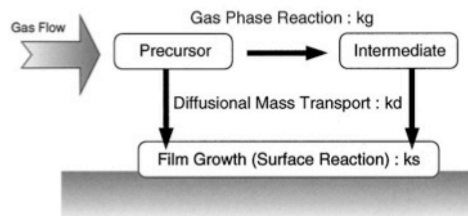


Fig. 17. Simplified CVD reaction mechanism.